The Stereochemistry of Addition Reactions of Allenes. II. Oxymercuration of 1,3-Dimethylallene and Solvolysis of the Derived Adducts

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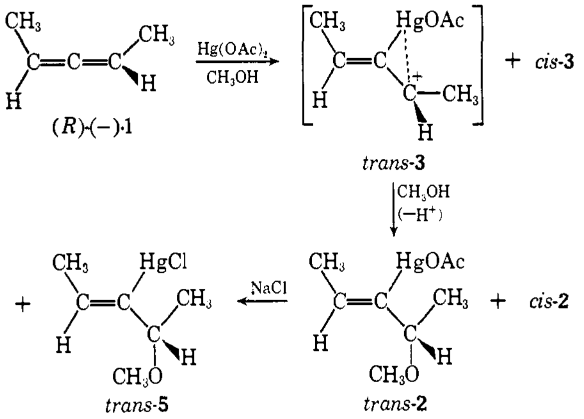
Abstract: In order to determine the stereospecificity of oxymercuration of 1,3-dimethylallene, the reverse reaction of deoxymercuration was studied. Both methoxymercuration of (−)-1,3-dimethylallene with mercuric chloride and deoxymercuration of the derived 3-chloromercuri-4-methoxy-2-pentene adducts were found to be nonstereospecific. Attempts to deoxymercurate 3-acetoxymercuri-4-methoxy-2-pentene were unsuccessful. The rates of acid-catalyzed reacemization and solvolysis of 3-acetoxymercuri- and 3-chloromercuri-4-acetoxy-2-pentene in methanol were measured and compared with the rates of the corresponding reactions of 4-acetoxy-2-pentene. The rates of racemization of the related methyl ether derivatives were also studied. The solvolytic and polarimetric data obtained for the oxymercurials do not support the intervention of dissymmetric mercurinium ion intermediates but conform closely to the behavior expected of symmetrical allylic ions. The implications of these results as they relate to the mechanisms of oxymercuration of allenes are discussed.

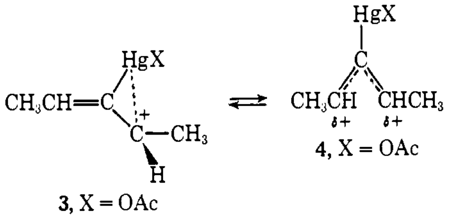
In previous work, the methoxymercuration of 1,3-dimethylallene (**1**) with mercuric acetate in methanol was shown to be a stereoselective *trans* addition[3] leading to 3-acetoxymercuri-4-methoxy-2-pentene (**2**) as a mixture of *cis* and *trans* isomers.[4,5] The mechanism proposed for the reaction[3,4] involves initial attack of the mercury electrophile to give dissymmetric mercurinium ions **3** which subsequently collapse to products by *trans*-rearward attack of the nucleophilic solvent at the methyl-substituted carbon (Scheme I).[5,6]

Scheme I



The recent work of Bach[7] on the oxymercuration of optically active 1,2-cyclononadiene is also consistent with the formation of dissymmetric mercurium ions, although the interesting observation was made that the stereospecificity of reaction and hence the importance of dissymmetric intermediates are dependent on the mercuric salt used.

The electron distribution in mercurinium ion intermediates is not really known. The work of Halpern and Tinker[8] on the kinetics of oxymercuration of alkenes does show, however, that the transition state has appreciable carbonium ion character. In view of this, mercurinium ions of type **3** are represented in this paper as unsymmetrically bridged species σ bonded to the central allenic carbon. The stability of **3** relative to its symmetrical allylic counterpart **4** (eq 1) is not known since the stereospecificity of methoxymercuration of **1** with mercuric acetate has not been determined. An estimate of the optical purity of (*R*)-(−)−**1** based on



(1)

Brewster's calculated value for the rotation of **1**[9] together with the optical purity determined for **2** obtained by oxymercuration of **1**[3] suggests that the reaction is highly, if not completely, stereospecific. However, an independent measure of the stereospecificity was considered desirable, and it was this objective that led to the work described in the present paper.

Deoxymercuration is the formation of alkenes from oxymercurials, and is essentially the reverse of oxymercuration. This type of reaction has been thoroughly investigated from the mechanistic standpoint by Kreevoy and coworkers.[10–19] Evidence accumulated

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(1) National Science Foundation Predoctoral Fellow, 1967–1969.

(2) To whom all correspondence should be addressed.

(3) W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, 90, 6741 (1968).

(4) W. L. Waters and E. F. Kiefer, *ibid.*, 89, 6261 (1967).

(5) The major product is the *trans* isomer (83%). Unless otherwise stated all the oxymercurials employed in this work were 17:83 mixtures of *cis* and *trans* isomers. To conserve space and retain clarity, only the reactions of the *trans* isomers are given in detail in the formulas and equations in this paper. The comparable reactions of the *cis* isomers are assumed.

(6) An excellent review of oxymetallation reactions has recently been published: W. Kitching, *Organometal. Chem. Rev.*, 3, 61 (1968).

(7) R. D. Bach, *J. Amer. Chem. Soc.*, 91, 1771 (1969); R. D. Bach, *Tetrahedron Lett.*, 5841 (1968).

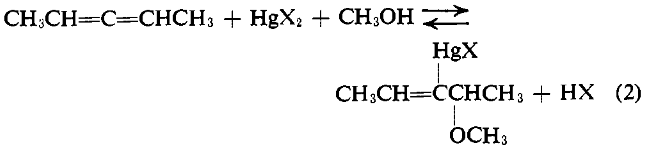
(8) J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, 89, 6427 (1967).

(9) J. H. Brewster in "Topics in Stereochemistry," Vol. 2, N. L. Allinger and E. L. Eliel, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967.

(10) M. M. Kreevoy, G. Stokker, R. A. Kretchmer, and A. K. Ahmed, *J. Org. Chem.*, 28, 3184 (1963).

(11) M. M. Kreevoy, J. W. Gilje, L. T. Ditsch, W. Batorewicz, and M. A. Turner, *ibid.*, 27, 726 (1962).

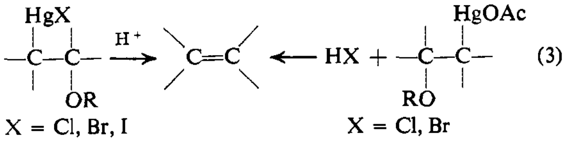
from kinetic data,[10–13,20,21] the dependence of reactivity on structure,[14,15] secondary deuterium isotope effects,[16,17] and solvent effects[18,19] relating to the deoxymercuration of β-alkoxy-α-halomercurials has led to the conclusion that mercurinium ions are formed from the protonated oxymercurial in the rate-determining step. In the present work, we reasoned that if deoxymercuration of **2** could be achieved by way of mercurinium ions **3** and **4** then the change in optical rotation of (*R*)-(−)-**1** recovered after an oxymercuration–deoxymercuration sequence (eq 2) could serve as a measure of the stereospecificity of reaction in either direction.



$$CH_3CH{=}C{=}CHCH_3 + HgX_2 + CH_3OH \rightleftarrows CH_3CH{=}\underset{OCH_3}{\overset{HgX}{C}}CHCH_3 + HX \quad (2)$$

As will shortly be described, conditions of microscopic reversibility for the allene–mercuric acetate system were not found, but the results obtained concerning the optical stability of oxymercurials derived from **1** can be related to the nature of the mercurinium ions which are postulated as intermediates in the oxymercuration of **1**.

Deoxymercuration. Formation of alkenes from oxymercurials usually requires strong acid and halide ions[10–22] present either as the acidic component or as covalently bonded ligands on mercury (eq 3). For



$$\underset{OR}{\overset{HgX}{-C-C-}} \xrightarrow{H^+} {>}C{=}C{<} \longleftarrow HX + -\underset{RO}{C}-\overset{HgOAc}{C}- \quad (3)$$

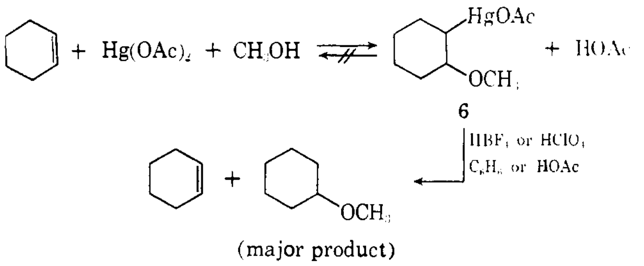
X = Cl, Br, I   X = Cl, Br

this reason, our initial study of the deoxymercuration of oxymercurials derived from **1** was confined to the *cis* and *trans* chloromercuri adducts **5**. These were obtained from the corresponding acetoxymercuri adducts **2** by treatment with aqueous sodium chloride (Scheme I). Waters and Kiefer[4] have previously reported that β-methoxy-α-chloromercuri adducts of allenes deoxymercurate in cold concentrated hydrochloric acid to the parent allene. On shaking a solution of optically active **5** in benzene with excess hydrochloric acid at 0°, 1,3-dimethylallene was the *only* hydrocarbon formed. However, it was found to be *racemic*. Furthermore, unreacted mercurials recovered from reaction mixtures initially containing less than 1 equiv of acid were found to be extensively racemized. Active allene, (*R*)-(−)-**1**, was optically stable in the benzene–hydrochloric acid mixture over many half-lives of the mercurial **5**, but addition of methanolic mercuric chloride resulted in rapid racemization of **1**. We conclude, therefore, that deoxymercuration of **5** is a nonstereospecific process. Equally, the reverse reaction of oxymercuration of 1 with methanolic mercuric chloride is nonstereospecific (eq 2, X = Cl). These results are consistent with the observations reported by Bach[7] on the oxymercuration of 1,2-cyclononadiene with mercuric chloride, which he found to be essentially nonstereospecific.

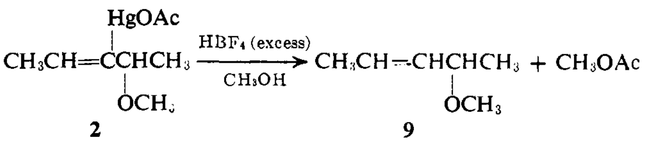
Since the stereospecificity of reaction with mercuric chloride is clearly different from that with mercuric acetate,[3,7] we decided to investigate the deoxymercuration of the acetoxymercurials **2**. We have already alluded to the apparent fact that oxymercuration of alkenes is irreversible in the absence of halide ions or halomercuri derivatives. Evidence for this stems from the optical stability of 2-methoxy-1-acetoxymercuricyclohexane **6** in methanol and acetic acid[23] (Scheme II), and from the observation that 2-hydroxy-1-nitromercuriethane **7** does not eliminate to give ethylene in 5% sulfuric acid but gives instead the bisether **8**.[24] Nevertheless, we investigated the reaction of **6** with strong acid (HBF_4 or $HClO_4$) in both benzene and glacial acetic acid. Cyclohexene was indeed formed, but in low yield, the main product being cyclohexyl methyl ether (Scheme II).

$$\underset{\mathbf{7}}{2HOCH_2CH_2HgNO_3} \xrightarrow{5\%\ H_2SO_4} \underset{\mathbf{8}}{O(CH_2CH_2HgNO_3)_2} + H_2O$$

Scheme II



Similarly, attempts to deoxymercurate **2** in methanol containing excess fluoroboric acid were unsuccessful. 1,3-Dimethylallene was not formed, but demercuration took place to give 4-methoxy-2-pentene **9** (eq 4). While



$$CH_3CH{=}\underset{OCH_3}{\overset{HgOAc}{C}}CHCH_3 \xrightarrow[CH_3OH]{HBF_4\,(excess)} CH_3CH{=}CH\underset{OCH_3}{C}HCH_3 + CH_3OAc \quad (4)$$

2   **9**

other solvent systems might favor deoxymercuration, methanol was the only solvent used in the present study since the main objective was to simulate conditions used in the methoxymercuration of **1**[3] as closely as possible. Failure to observe deoxymercuration of the methoxy adducts **2** led to a study of the behavior of the corresponding acetates **10** in the hope that deoxymercuration may be promoted in the presence of a better leaving group.

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(12) M. M. Kreevoy and F. R. Kowitt, *J. Amer. Chem. Soc.*, **82**, 739 (1960).
(13) M. M. Kreevoy, *ibid.*, **81**, 1099 (1959).
(14) M. M. Kreevoy and M. A. Turner, *J. Org. Chem.*, 30, 373 (1965).
(15) L. L. Schaleger, M. A. Turner, T. C. Chamberlin, and M. M. Kreevoy, *ibid.*, 27, 3421 (1962).
(16) M. M. Kreevoy and B. M. Eisen, *ibid.*, **28**, 2104 (1963).
(17) M. M. Kreevoy and L. T. Ditsch, *J. Amer. Chem. Soc.*, **82**, 6127 (1960).
(18) M. M. Kreevoy, J. W. Gilje, and R. A. Kretchmer, *ibid.*, **83**, 4205 (1961).
(19) M. M. Kreevoy and L. T. Ditsch, *J. Org. Chem.*, **25**, 134 (1960).
(20) K. Ichikawa, K. Nishimura, and S. Takayama, *ibid.*, 30, 1593 (1965).
(21) K. Ichikawa, H. Ouchi, and S. Araki, *J. Amer. Chem. Soc.*, **82**, 3880 (1960).
(22) J. Chatt, *Chem. Rev.*, **48**, 7 (1951).
(23) J. Romeyn and G. F. Wright, *J. Amer. Chem. Soc.*, **69**, 697 (1947); W. H. Brown and G. F. Wright, *ibid.*, 62, 1991 (1940).
(24) J. Sand, *Ann. Chem.*, **329**, 135 (1903).

Table I. Specific Rotation Data for the Oxymercurials Obtained from (*R*)-(−)-1,3-Dimethylallene[a]

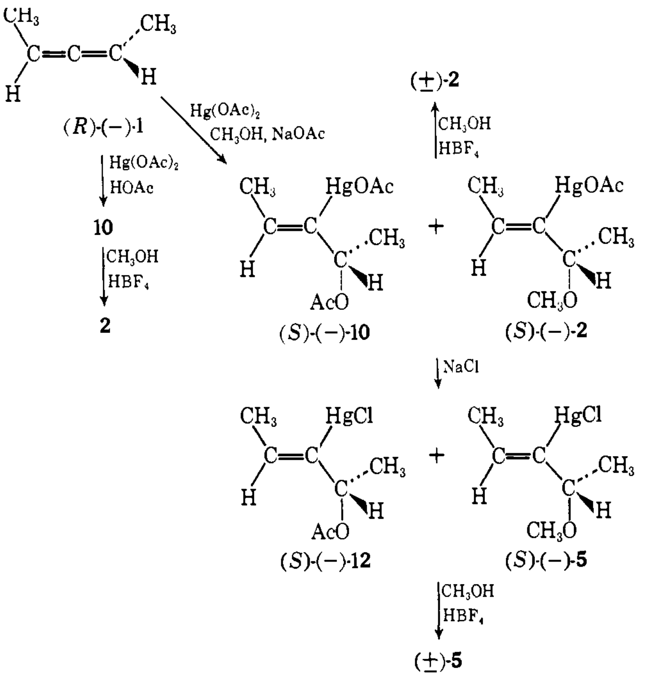
1[b]	**2**[c]	**5**[c]	**2 + 10**[c,d]	**5 + 12**[c,d]	**10**[e]	**12**[e]
19.1	4.67 ± 0.25	5.20 ± 0.10				
19.1	[4.67][f]		7.09 ± 0.50 (36:64)		8.3	
19.1	[4.67)[f]		7.58 ± 0.50 (48:52)		9.1	
15.3	4.30 ± 0.30	3.40 ± 0.60				
15.3	[4.30][f]		6.70 ± 0.40 (34:66)		8.8	
15.3	3.14 ± 0.20	3.69 ± 0.20				
15.3	[3.14][f]		5.90 ± 0.20 (46:54)		8.1	
15.3		[3.69][f]		4.88 ± 0.80 (43:57)		5.8

[a] Specific rotations of oxymercurials given are all minus degrees in $CHCl_3$. [b] In ether, error limits ±0.1°. [c] 1:4 *cis–trans* mixture. [d] Values in parentheses represent ratio of ether to ester. [e] Calulated from composition and rotation of ether–ester mixture and from specific rotation of ether prepared in the absence of NaOAc. [f] Value obtained in the absence of NaOAc.

Solvolysis Reactions. Kreevoy and coworkers have observed that solvolytic deoxymercuration of β-acetoxy-α-iodomercurials occurs readily in aqueous solvents.[25,26] The possibility that solvolysis of *cis*- and *trans*-3-acetoxymercuri-4-acetoxy-2-pentene **10** in methanol might also result in deoxymercuration was therefore considered. An 83:17 *trans–cis* mixture of **10** was prepared by the addition of mercuric acetate to **1** in acetic acid, and by the addition of mercuric acetate to **1** in methanol saturated with sodium acetate. By the latter method, a 50:50 mixture of acetates **10** and ethers **2** was obtained (Scheme III).

Methanol solutions of **10** were found to be stable, but on addition of catalytic amounts of fluoroboric acid solvolysis occurred to give an 83:17 *trans–cis* mixture of methyl ethers **2** (Scheme III). *Deoxymercuration was not observed.*

Scheme III



While this result proved negative as far as regenerating the parent allene, methanolysis of **10** presumably involves the formation of ionic intermediates that may be related to the intermediates formed in the methoxymercuration of **1**. Thus, if bridged mercurinium ions **3** participate in the solvolysis of **10**, the methyl ethers **2** may be expected to be formed stereospecifically with retention of configuration. To test this supposition, a study was made of the kinetics of acid-catalyzed solvolysis and racemization of the acetates and methyl ethers derived from oxymercuration of optically active **1**. Related data on the solvolysis and racemization of the simple allylic derivatives, 4-methoxy-2-pentene **9** and 4-acetoxy-2-pentene **11**, were also obtained in order to evaluate the effect of the neighboring vinylic mercury substituent on the rates of solvolysis and racemization of the oxymercurials.

Since optically active **10** could not be isolated from reaction of **1** with mercuric acetate in acetic acid, active **10** was prepared as a mixture with **2** by oxymercuration of **1** in methanol saturated with sodium acetate (Scheme III). The specific rotation of **10** present in the mixture was calculated from the observed rotation and the per cent composition of the mixture, and from the specific rotation of the methyl ethers **2**. The assumption was made that the specific rotation of **2** in the mixture was the same as that for **2** produced in the methoxymercuration of **1** in the absence of added sodium acetate. A summary of the rotation data obtained is given in Table I.

The acetoxymercurials **2** and **10** were converted to the corresponding chloromercurials **5** and **12** by treatment with aqueous sodium chloride (Scheme III). The specific rotation of **12** was calculated as for **10**, again assuming that the specific rotation of the methyl ether **5** was equal to that produced by the reaction sequence of Scheme I (*cf.* Table I). Acid-catalyzed solvolysis of the chloromercurial **12** resembled the acetoxymercurial and led neither to deoxymercuration nor demercuration but gave an 83:17 mixture of *trans* and *cis* methyl ethers **5** (Scheme III).

Synthesis of optically active *trans*-4-acetoxy-2-pentene **11** was achieved by the reaction of partially resolved (*R*)-(−)-*trans*-3-penten-2-ol[27] (**13**) with acetyl chloride and N,N-dimethylaniline in ether. The methyl ether **9** was prepared from (*R*)-(−)-**13** as described previously[3] (Scheme IV).

Solvolysis of (+)-**11** was anticipated to proceed typically by alkyl-oxygen cleavage to give symmetrical α,γ-dimethylallyl cations leading to racemic products.[26–31] Methanolysis in the presence of fluoroboric

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[25] M. M. Kreevoy and G. B. Bodem, *J. Org. Chem.*, **27**, 4539 (1962).

[26] M. M. Kreevoy and M. A. Turner, *ibid.*, **29**, 1639 (1964).

[27] (a) H. W. J. Hills, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 576 (1936); (b) P. A. Levene and H. L. Haller, *J. Biol. Chem.*, **81**, 703 (1929).

[28] M. P. Balfe, H. W. J. Hills, J. Kenyon, H. Phillips, and B. C. Platt, *J. Chem. Soc.*, 556 (1942).

[29] H. L. Goering and R. W. Greiner, *J. Amer. Chem. Soc.*, **79**, 3464 (1957).

[30] H. L. Goering and M. M. Pombo, *ibid.*, **82**, 2515 (1960).

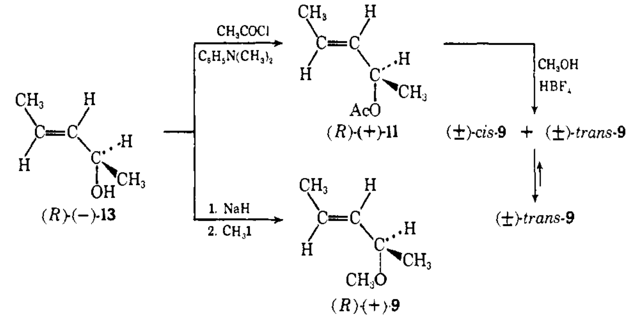
Table II. Rate Data for Solvolysis and Racemization of Derivatives of 2-Pentene, $CH_3CH{=}\overset{X}{\overset{|}{C}}{-}\underset{OR}{\underset{|}{C}}HCH_3$, in Methanol, 0.060 *M* in HBF$_4$, at 28°

Substrate	X	OR	[Substrate], *M*	k_{rac}, hr^{-1}	$t^{1/2}$, hr	k_{sol}, hr^{-1}	$t^{1/2}$, hr
2	HgOAc	OCH$_3$	0.70	0.0058	120		
5	HgCl	OCH$_3$	0.44	0.29	2.4		
9	H	OCH$_3$	0.50	0.0038	180		
10	HgOAc	OAc	0.54^a	0.05^b	14^b	0.027	26
10	HgOAc	OAc	0.54^a			0.030	23
12	HgCl	OAc	0.20^c	0.4^b	1.7^b	0.15	4.5
12	HgCl	OAc	0.20^c			0.18	3.9
11	H	OAc	0.50	0.0554	12.5	0.0447	15.5
11	H	OAc	0.50	0.0537	12.9	0.0453	15.3

[a] Reaction mixture was initially 0.46 *M* in **2**. [b] Calculated from eq 5 assuming $\alpha_x = 0$ and using the independently measured value of k_{rac} for **2** or **5** but replacing k_{sol} by k_{rac} of **10** or **12**. [c] Reaction mixture was initially 0.15 *M* in **5**.

acid did indeed give racemic **9**, but in following the reaction by nmr, it was observed that a mixture of *cis*- and *trans*-**9** was initially formed, and the *cis* isomer slowly rearranged under the reaction conditions to the more stable *trans* isomer.[32] This observation is more fully discussed later.

Scheme IV



Kinetic Results. In the kinetic experiments, methanolysis of the acetate esters **10, 11,** and **12** was uniformly carried out in methanol solutions 0.5 *M* in substrate and 0.060 *M* in fluoroboric acid at 28°. The solvolysis rates were followed by nmr (see Experimental Section) and the accompanying loss of optical activity was followed polarimetrically. The rates of racemization of the methyl ethers **2, 5,** and **9** were also determined in methanol solutions 0.06 *M* in fluoroboric acid. The kinetic data obtained are summarized in Table II and Figures 1–4.

The following points may be noted. Racemization of the methyl ethers **2**, **5**, and **9** followed reasonably good first-order kinetics (Figure 1) and the relative rates show that the acetoxymercurial **2** does not racemize appreciably faster than the nonmercurated derivative **9**, although the chloromercurial **5** racemizes 76 times faster than **9** (Table II). Methanolysis of the esters **10, 11,** and **12** also obeyed first-order kinetics (Figure 2), and again the rates of the acetoxymercurial **10** and the nonmercurated ester **11** are comparable while the chloromercurial **12** reacts some four times faster than **11** (Table II). The most significant feature of the kinetic data is the optical rotation behavior observed for both the acetoxymercurial mixture **10** and **2** and the chloromercurial mixture **12** and **5**. The polarimetric rates are *faster* than the rates of solvolysis of the corresponding esters and the rates of racemization of the ethers (Figures 3 and 4). The mechanistic implications of these results are more fully discussed in the next section.

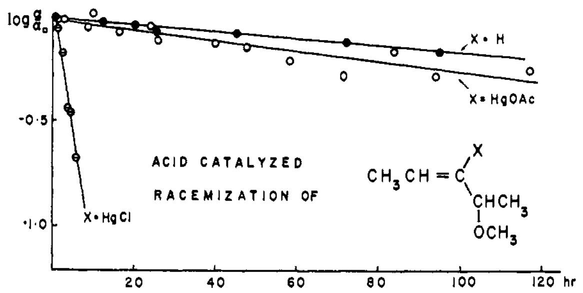


Figure 1. Rates of racemization of 4-methoxy-2-pentene derivatives in methanol, 0.060 *M* in HBF$_4$, at 28°.

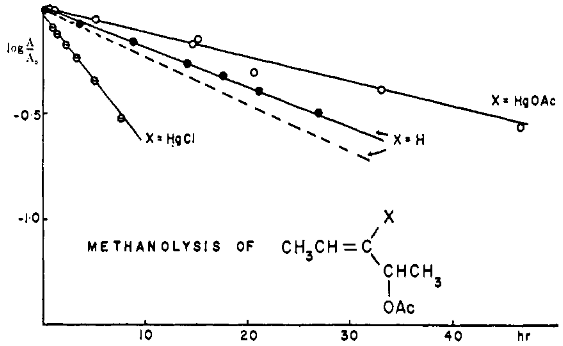


Figure 2. Rates of methanolysis of 4-acetoxy-2-pentene derivatives, 0.060 *M* in HBF$_4$ at 28° as measured by nmr. The term A/A_0 is the ratio of unreacted substrate to that initially present. The dashed line represents the rate of racemization of (+)-4-acetoxy-2-pentene under the solvolysis conditions.

Discussion

The observation that the rates of acid-catalyzed racemization and solvolysis of the acetoxymercuri

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(31) H. L. Goering, M. M. Pombo, and K. D. McMichael, *J. Amer. Chem. Soc.*, **85**, 965 (1963).

(32) The possibility of acyl–oxygen cleavage in the solvolysis of **11** to produce the alcohol **13** which would subsequently react to give the ether **9** was disproven by following the methanolysis of **11** by glpc. The ether peak **9** was observed to build up at a rate concomitant with the decrease of that due to the starting ester **11**. No evidence was obtained that the allylic alcohol **13** was formed.

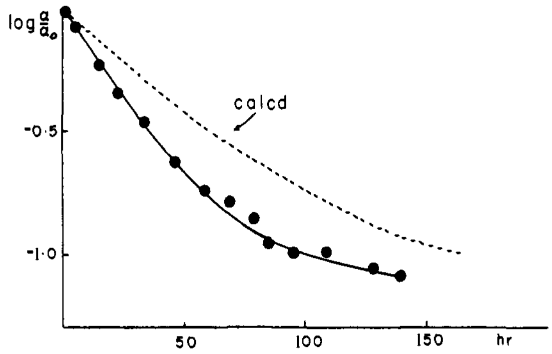


Figure 3. Rate of racemization of a 54:46 mole per cent mixture of 4-acetoxy- and 4-methoxy-3-acetoxymercuri-2-pentenes, **10** and **2**, in methanol, 0.060 M in HBF_4, at 28°. The dashed curve is that calculated from eq 5 assuming $\alpha_x = 0$, k_{rac} of **2** as 5.8×10^{-3} hr^{-1} and k_{sol} of **10** as 2.7×10^{-2} hr^{-1}.

derivatives **2** and **10** are not significantly different from the rates of the corresponding reactions of the simple allylic derivatives **9** and **11** suggests that there is no participation of the neighboring acetoxymercuri substituent in the transition states for racemization of **2** and solvolysis of **10**. The rate data do not support the intervention of bridged mercurinium ions of the type proposed as intermediates in the methoxymercuration of **1** with mercuric acetate (*i.e.*, **3**). If bridged intermediates are involved, solvolysis of **10** may be expected to proceed with retention of configuration, and the observed rotation (α) of the reaction mixture should follow the rate law given in eq 5. In this equation, k_{sol} and k_{rac} represent the specific rates of solvolysis of **10** and racemization of **2**, respectively, both of which were independently determined (Table II). The mole fractions of **10** and **2** are given by N_{OAc} and N_{OCH_3}, respectively, and the initial rotations α_{OAc} and α_{OCH_3} are normalized such that $\alpha = \alpha_{OAc}N_{OAc} + \alpha_{OCH_3} \cdot N_{OCH_3}$ at zero time. The term in α_x reflects the stereochemistry and stereospecificity of solvolysis. It essentially represents the buildup and decay of optically active **2** produced in the solvolysis of **10**. For stereospecific solvolysis with retention of configuration, $\alpha_x = \alpha_{OCH_3}$. For nonstereospecific solvolysis, $\alpha_x = 0$, and the rate law reduces to the sum of two straightforward first-order processes. The experimental rate (Figure 3) does not conform to eq 5 for either $\alpha_x = \alpha_{OCH_3}$, or $\alpha_x = 0$. The observed rotation, α, actually decreases more *rapidly than* predicted for a nonstereospecific process for which $\alpha_x = 0$. This behavior is reminiscent of that observed for the uncatalyzed solvolysis of esters of 3-penten-2-ol which has been extensively studied by Goering and coworkers.[29-31] These investigators have obtained convincing evidence that solvolysis proceeds by way of symmetrical ion-pair intermediates that either collapse to racemic ester or react with the hydroxylic solvent to give racemic products. This process accounts for the fact that rates of racemization are faster than rates of solvolysis. However, there are no ion-pair intermediates in the acid-catalyzed solvolysis of **10** although on dissociation the allylic ion **4** may possibly remain proximate to the neutral leaving group, which is a molecule of acetic acid, such that a significant fraction of the allylic ions return to the starting ester. Internal return involving an ion and a neutral molecule is not unprecedented since Goering and Dilgren[33] have demonstrated by oxygen-exchange studies associated with the acid-catalyzed rearrangement of α-phenylallyl alcohol that ion–molecule internal return competes effectively with ion–solvent reaction.[34]

$$\alpha = \alpha_{OAc}N_{OAc}e^{-k_{sol}t} + \alpha_{OCH_3}N_{OCH_3}e^{-k_{rac}t} + \alpha_x \frac{N_{OAc}k_{sol}}{(k_{rac} - k_{sol})}(e^{-k_{sol}t} - e^{-k_{rac}t}) \quad (5)$$

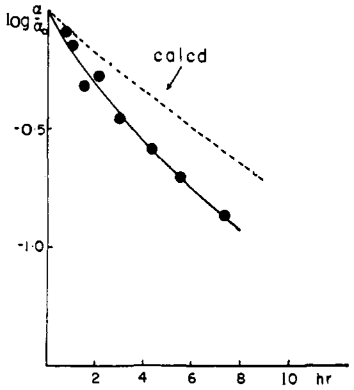
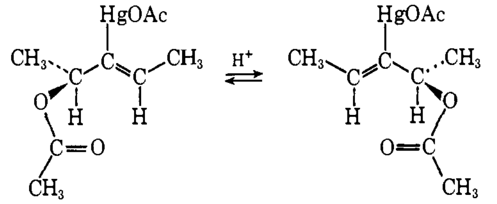


Figure 4. Rate of racemization of a 57:43 mole per cent mixture of 4-acetoxy- and 4-methoxy-3-chloromercuri-2-pentenes, **12** and **5**, in methanol, 0.060 M in HBF_4, at 28°. The dashed curve is that calculated from eq 5 assuming $\alpha_x = 0$, k_{rac} of **5** as 0.29 hr^{-1} and k_{sol} of **12** as 0.15 hr^{-1}.

The polarimetric data could also be explained by an acid-catalyzed SNi′ concerted rearrangement proceeding with retention of geometric configuration but inversion of optical configuration (eq 6), but in the absence of labeling studies, this process cannot be distinguished from one involving dissociation followed by internal return.



(6)

(*S*)-(−)-**10** (*R*)-(+)-**10**

The solvolytic behavior of the chloromercurial **12** is similar to that of the acetoxymercurial **10**. Racemization takes place more rapidly than solvolysis (Figure 4 and Table II) which implies that symmetrical allylic intermediates rather than dissymmetric or bridged ions are involved. This result is less surprising for the chloromercuri derivatives than for the acetoxymercuri derivatives since the low stereospecificity of oxymercuration of allenes with mercuric chloride suggests that bridged chloromercurinium ions, if formed at all, rapidly convert to symmetrical ions.[7] However, the solvolysis of **12** and the racemization of **5** are appreciably faster than the corresponding reactions of the acetoxymercurials and the 3-penten-2-ol derivatives. While we can offer no convincing explanation for the

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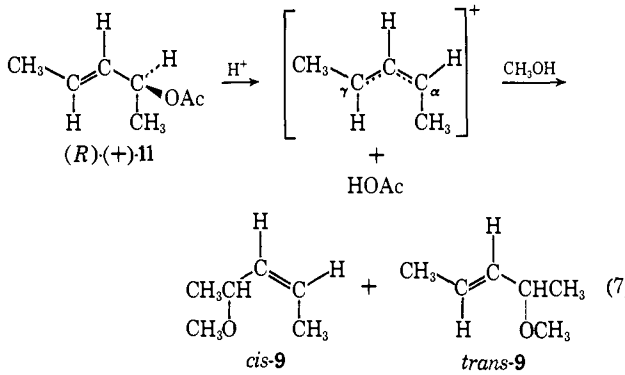
(33) H. L. Goering and R. E. Dilgren, *J. Amer. Chem. Soc.*, **82**, 5744 (1960).

(34) See also the report on ion–molecule internal return in the solvolysis of *p*-methoxybenzylethylmethylsulfonium perchlorate by D. Darwish, S. H. Hui, and R. Tomilson, *ibid.*, **90**, 5631 (1968).

rate differences observed, we accept the data as providing additional evidence that the ligand on mercury has a profound effect on both the stereochemistry of oxymercuration of allenes and on the rates of solvolysis of the derived adducts.

The polarimetric data for the nonmercurated ester **11** show that the rate of acid-catalyzed racemization is slightly greater than the rate of solvolysis. This result is consistent with dissociation to the α,γ-dimethylallyl ion followed by some internal return to the starting ester accompanying solvolysis to the methyl ether **9**. Formation of the *cis* ether as well as the *trans* ether implies that the ester may react in the conformation shown in eq 7 with attack of solvent occurring at the γ position to give the *cis* ether, and at the α position to give the *trans* ether. But the possibility of an SN2′ contribution to the reaction such as that observed by Goering and Josephson in the acid-catalyzed rearrangement of *trans*-5-methyl-2-cyclohexanol[35] cannot be excluded.



(*R*)-(+)-**11**

cis-**9** *trans*-**9** (7)

Solvolysis of the acetoxymercurial **10** is evidently a poor model for the oxymercuration of **1** with mercuric acetate since different intermediates are involved in the two reactions. Our initial objective of determining the stereospecificity of oxymercuration of **1** was not therefore achieved. However, the results do allow some conclusions to be made concerning the energetics of the various steps involved in oxymercuration. With reference to the energy diagram of Figure 5 (which represents the reaction coordinates for oxymercuration–deoxymercuration and solvolysis), for oxymercuration of **1** with mercuric acetate to be a stereospecific *trans* addition, the initially formed mercurinium ion must be dissymmetric (**3**) and must react with solvent *faster* than it can convert to the open ion **4** (*i.e.*, B < C). For the acid-catalyzed solvolysis of acetoxymercurials derived from **1** to proceed by way of open ions **4**, the transition state leading to **4** must be lower in energy than that leading to **3** (*i.e.*, D < B). This does not necessarily mean that open ions **4** are more stable than bridged ions **3**, as shown in Figure 5, although this is very probably the case.[36]

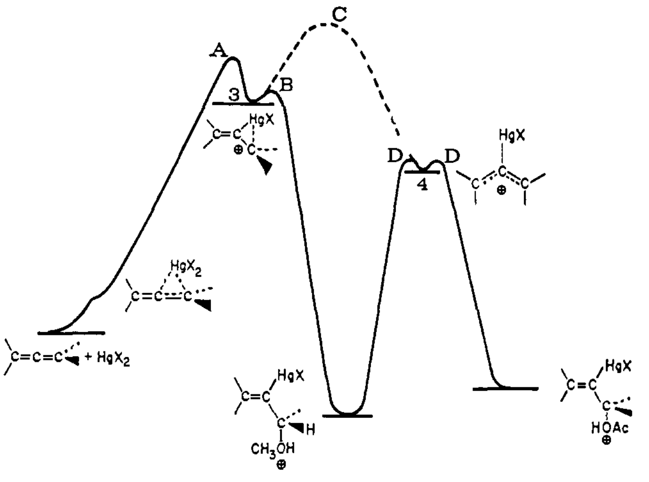


Figure 5. Reaction profile for the methoxymercuration of allenes and solvolysis of acetoxy and methoxy mercurial adducts.

While the unsymmetrically bridged ion **3** most closely resembles the transition state for methoxymercuration of **1** with mercuric acetate, the extent of C–O bond making in the transition state is not easily determined.[37] Based on the deoxymercuration studies of Kreevoy and coworkers,[10–19] the rate-determining step in oxymercuration is expected to be the reaction of **3** with solvent (*i.e.*, B > A, Figure 5). If this were the case, the *cis–trans* ratio of oxymercurial adducts obtained from **1** would be expected to vary with the nature of the solvent. However, we have found that this ratio is essentially invariant over the range of solvents studied, which includes methanol, acetic acid, isopropyl alcohol,[38] and *t*-butyl alcohol.[38] We regard this as evidence that C–O bond formation is kinetically insignificant in the oxymercuration of **1** with mercuric acetate and hence that the rate-determining step is the formation of mercurinium ions **3** (A > B, Figure 5).

Finally, for oxymercuration of **1** with mercuric chloride to be nonstereospecific, the energy barrier to interconversion of bridged and open ions must be considerably lower than in the acetoxymercuri analogs. If in fact the energy barrier C of Figure 5 is sufficiently low when X = Cl, then C becomes the transition state for oxymercuration of **1** with mercuric chloride and the question of bridged ions as reaction intermediates is academic.

Experimental Section

Methoxymercuration of (*R*)-(−)-1,3-Dimethylallene (1). The preparation and partial resolution of **1** were performed as described previously.[3] It is important in the resolution step that **1** be added as rapidly as possible to the diisopinocampheyldiborane mixture since slow addition may result in the recovery of racemic **1**. The addition of mercuric acetate to (*R*)-(−)-**1** was carried out as described previously.[3] After neutralization of the reaction mixture with sodium carbonate and evaporation of the solvent, the residue was extracted with methylene chloride and the extract evaporated to give an 83:17 mixture of *trans*- and *cis*-4-methoxy-3-acetoxymercuri-2-pentene **2** as a viscous oil. For the preparation of 4-methoxy-3-chloromercuri-2-pentene **5**, 1 equiv of aqueous sodi-

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(35) H. L. Goering and R. R. Josephson, *J. Amer. Chem. Soc.*, **83**, 2585 (1961).

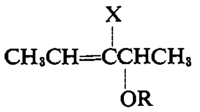
(36) Failure to form bridged bromonium ions from dibromo adducts of **1** has been noted previously[3] and is analogous to the present example of solvolysis of mercurial adducts of **1**. Bromination of *R*-(−)-**1** in methanol gave optically active 3-bromo-4-methoxy-2-pentene and 3,4-dibromo-2-pentene. Methanolysis of the active dibromo adduct with silver nitrate gave essentially racemic 3-bromo-4-methoxy-2-pentene, indicating the intermediacy of open allylic ions.

A reaction of some interest and relevance to the present results is the methanolysis of optically active *trans*-chloromercuri-2-acetoxycyclooctane which is reported to give *trans*-chloromercuri-2-methoxycyclooctane with partial retention of optical activity (V. I. Sokolov, L. L. Troitskaya, and O. A. Reutov, *J. Organometal. Chem.*, **17**, 323 (1969)). As the authors point out, this result excludes the possibility that the solvolysis product is derived solely from a symmetrical mercurinium ion intermediate.

(37) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(38) Unpublished work, W. L. Waters.

Table III. Nmr Spectral Parameters for 2-Pentene Derivatives[a]



$$CH_3CH{=}\overset{X}{\underset{OR}{C}}CHCH_3$$

Compd	X	OR	δ_{1-CH_3}, ppm	J, Hz	δ_{5-CH_3}, ppm	J, Hz	δ_{OR}, ppm	δ_X, ppm	δ_{2-H}, ppm	δ_{4-H}, ppm	Solvent
trans-**2**	HgOAc	OCH_3	1.97 (d)	6.0	1.16 (d)	6.3	3.15 (s)	1.95 (s)	6.14 (q)	3.41 (q)	$CHCl_3$
cis-**2**	HgOAc	OCH_3	1.97 (d)	6.0	1.13 (d)	6.3	3.18 (s)	1.95 (s)	6.1 (q)	*b*	$CHCl_3$
trans-**5**	HgCl	OCH_3	1.87 (d)	6.5	1.22 (d)	6.1	3.22 (s)		6.33 (q)	3.90 (q)	$CHCl_3$
cis-**5**	HgCl	OCH_3	1.87 (d)	6.5	1.18 (d)	6.1	3.26 (s)		6.3 (q)	*b*	$CHCl_3$
trans-**10**	HgOAc	OAc	1.82 (d)	6.3	1.25 (d)	6.3	2.0 (s)	2.0 (s)	6.23 (q)	5.5 (q)	$CHCl_3$
cis-**10**	HgOAc	OAc	1.82 (d)	6.3	1.23 (d)	6.3	2.0 (s)	2.0 (s)	6.2 (q)	*b*	$CHCl_3$
trans-**12**	HgCl	OAc	1.85 (d)	6.3	1.31 (d)	6.3	2.0 (s)		6.45 (q)	5.50 (q)	$CHCl_3$
cis-**12**	HgCl	OAc	1.85 (d)	6.3	1.25 (d)	6.3	2.0 (s)		6.4 (q)	*b*	$CHCl_3$
trans-**9**[c]	H	OCH_3	1.66 (d)	5.3	1.13 (d)	6.5	3.12 (s)	5.4 (m)	5.4 (m)	3.52 (m)	CCl_4
trans-**11**	H	OAc	1.67 (d)	5.3	1.26 (d)	6.5	1.98 (s)	5.6 (m)	5.6 (m)	5.3 (m)	$CDCl_3$

[a] Spectra were recorded using a Varian A56/60 spectrometer. Chemical shifts are in parts per million downfield from tetramethylsilane. The multiplicity of signals is given in parentheses. [b] This signal is not clearly resolved in the mixtures of *cis* and *trans* isomers employed, and chemical shift is uncertain. [c] *cis*-**9** formed in the methanolysis of *trans*-**11** shows δ_{5-CH_3} 0.08 ppm downfield of δ_{5-CH_3} of *trans*-**9**.

um chloride was added to the reaction mixture along with the sodium carbonate. After stirring for 30 min, the product was isolated as described for **2**. The nmr spectra of **2** and **5** are summarized in Table III.

4-Acetoxy-3-acetoxymercuri-2-pentene (10). Mercuric acetate (0.63 g, 2 mmol) was suspended in 8 ml of glacial acetic acid. To the stirred mixture was added 0.14 g (2.1 mmol) of **1** in ether. The mercuric acetate dissolved within 2 min and stirring was continued for a further 5 min after which time the solvents were removed at reduced pressure. The product, 0.39 g (50%), was obtained as a yellow oil. Its nmr spectrum is summarized in Table III. From the ratio of the allylic methyl doublets centered at 1.23 ppm (*cis* isomer) and 1.25 ppm (*trans* isomer), the product was established as a 1:4 mixture of *cis* and *trans* isomers.

Optically active **10** was prepared as a mixture with **2** by the following procedure. Sodium acetate (0.08 g, 1 mmol) and mercuric acetate (0.64 g, 2 mmol) were dissolved in 8 ml of methanol. 1,3-Dimethylallene (0.136 g, 2 mmol), $[\alpha]^{25}D$ −15.3° (*c* 34, ether), was added and the mixture stirred for 3 min. Sodium carbonate (0.21 g, 2 mmol) was then added and the mixture stirred for a further 10 min. The solvent was removed by evaporation at 1 mm and the residue was extracted with 20 ml of methylene chloride. The solvent was again removed leaving a viscous oil which was identified by nmr as an approximately equimolar mixture of 4-acetoxy- and 4-methoxy-3-acetoxymercuri-2-pentenes, **10** and **2**, respectively. The optical rotations of the mixtures obtained by this procedure are summarized in Table I. This mixture of **10** and **2** was converted to the corresponding chloromercurials **12** and **5** by the addition of aqueous sodium chloride.

Deoxymercuration of (−)-4-Methoxy-3-chloromercuri-2-pentene (5). To 1.0 g of **5**, $[\alpha]^{28}D$ −3.4° (*c* 10, $CHCl_3$), in 10 ml of benzene was added 1 equiv of concentrated hydrochloric acid at 0°. The mixture was shaken for 1 min; the benzene layer was separated, washed three times with dilute sodium bicarbonate solution, dried over magnesium sulfate, and filtered. Analysis of the filtrate by glpc and nmr showed the product to be 1,3-dimethylallene. The solution had no observable optical rotation. The experiment was repeated using 6.3 mmol of **5**, $[\alpha]^{27}D$ −4.8° (*c* 8, $CHCl_3$), and 3.2 mmol of hydrochloric acid in 10 ml of benzene. The mixture was worked up as before and the volatile components were removed by distillation at reduced pressure giving **1** (0.9 mmol) having no observable rotation. The residual solid was extracted with hot hexane to separate unreacted **5** from mercuric chloride. An 88% recovery of unreacted **5** was thereby obtained, $[\alpha]^{27}D$ −1.8° (*c* 10, $CHCl_3$).

On shaking 6 mmol of **1**, $[\alpha]^{25}D$ −18.7° (*c* 18, ether), with 2 equiv of hydrochloric acid in benzene for 4 min at 0°, no measurable change in the rotation of **1** was observed. Addition of 3 mmol of mercuric chloride to the acidified benzene mixture resulted in a 55% loss of optical activity after 10 min and complete loss of activity after 45 min. Analysis of the racemic mixture by glpc showed no change in the concentration of **1** and no additional volatile products. When 1 mmol of (−)-**1** in 7 ml of benzene was shaken with 0.5 mmol of mercuric chloride and 2 ml of methanol, the rotation decreased to 10% of its initial value within 10 min.

Deoxymercuration and Demercuration of 1-Acetoxymercuri-2-methoxycyclohexane (6). In Benzene. To 5 ml of benzene, 1 *M* in **6**, was added a slight excess of acid (70% $HClO_4$ or 50% HBF_4). Considerable tar formation was observed. Cyclohexene was found to be present in low concentration, but the reaction under those conditions was not further investigated.

In Methanol. To 5 ml of methanol, 1 *M* in **6**, was added dropwise a slight excess of 50% HBF_4 with stirring at room temperature. At 5-min intervals, a 0.5-ml sample was withdrawn, shaken with solid sodium carbonate, centrifuged, and analyzed by glpc. The major organic products were identified as cyclohexyl methyl ether and methyl acetate. A small amount (up to 5%) of cyclohexene was also formed.

Demercuration of 4-Methoxy-3-acetoxymercuri-2-pentene (2). Deoxymercuration of **2** was attempted in benzene and in methanol under the same conditions as described for **6**. In benzene, extensive tar formation occurred and no products were characterized. In methanol, the major organic reaction products were identified by glpc as 4-methoxy-2-pentene and methyl acetate. No 1,3-dimethylallene was detected.

(*R*)-(+)-4-Acetoxy-2-pentene (11). *trans*-3-Penten-2-ol[39] (**13**) was partially resolved in the usual way[27] and was estimated to be 39% optically pure and of the *R* configuration based on the specific rotation of its acid phthalate ester, $[\alpha]^{25}D$ −14.93° (*c* 6, $CHCl_3$).[40,41]

To 2.58 g (30 mmol) of (*R*)-(−)-**13** and 3.63 g (30 mmol) of N,N-dimethylaniline in 30 ml of anhydrous ether was added dropwise with stirring 2.36 g (30 mmol) of acetyl chloride in 15 ml of ether. After 10 min, the mixture appeared cloudy as the amine hydrochloride began to separate. The mixture was refluxed until glpc analysis of the reaction mixture indicated that all the reactant had been consumed (approximately 24 hr). The mixture was filtered and the ether removed by distillation through a small Vigreux column. The residue was distilled at reduced pressure and gave 2.1 g of **11**, bp 50° (23 mm), $[\alpha]^{26}D$ +32° (neat). In one preparation of **11**, traces of N,N-dimethylaniline were evidently present which resulted in a spuriously slow solvolysis rate. To eliminate the base, the ester was shaken with cold 1% hydrochloric acid, followed by repeated washing with water.

Kinetics of Racemization and Solvolysis. Methanolic solutions of optically active reagents were prepared from a stock methanol–fluoroboric acid solution such that each reaction mixture was 0.060 *M* in fluoroboric acid and approximately 0.5 *M* in reactant. A Zeiss polarimeter reading to ±0.01° was used to follow the rates of racemization of solutions maintained at 28°. In the solvolysis of the acetates **10**, **11**, and **12**, the initial reaction mixture (0.5 *M* in ester and 0.060 *M* in acid) was divided into two parts, one of which was observed by nmr, the other by polarimetry. In each case, the rate of solvolysis was followed by observing the changes

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(39) E. R. Coburn, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 696.

(40) H. L. Goering, M. M. Pombo, and K. D. McMichael, *J. Amer. Chem. Soc.*, **85**, 965 (1963).

(41) See footnote 18 in H. L. Goering and W. I. Kimoto, *ibid.*, **87**, 1748 (1965).

in the nmr spectrum of the ester with the probe temperature maintained at 28°. When not actually recording the spectrum, the sample was maintained at 28° in a constant-temperature bath. The region of the nmr spectrum used in determining the solvolysis rate was that of the allylic methyl resonances. By measuring the decrease in peak height or area of the *downfield* half of the allylic methyl doublet of the ester and the corresponding increase in the *upfield* half of the allylic methyl doublet of the ether product at appropriate time intervals, the pseudo-first-order solvolysis rate data summarized in Table II and Figure 2 were obtained.

Acknowledgment. The authors wish to acknowledge gratefully the support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society (PRF-2357-A1,4).

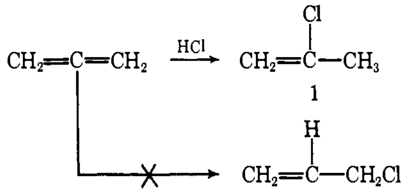
Stable Carbonium Ions. XCVI.[1a] Propadienylhalonium Ions and 2-Haloallyl Cations[1b]

J. Martin Bollinger, Jean M. Brinich,[1c] and George A. Olah

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received October 2, 1969*

Abstract: 2,3-Dihalopropenes in SbF_5–SO_2 solution form propadienylhalonium ions which were studied by nmr spectroscopy. These intermediates have recently been postulated to be responsible for the direction of halogen additions to allene and substituted allenes. We have also prepared and studied by nmr spectroscopy a series of 2-halopolymethylallyl cations which exist as nearly planar allyl cations. In some of these ions we have been able to measure free energies of activation for rotation.

Polar additions of hydrogen halides to allene yield 2-halopropenes (**1**) rather than 3-halopropenes (**2**).[2] The reason usually given for this result is that addition of a proton to the central carbon of allene does not give a resonance-stabilized allyl cation but rather one in which the p orbital of the carbonium ion carbon is orthogonal to the p orbital of the double bond (**3**). Apparently this ion is less stable than the vinyl cation (**4**).



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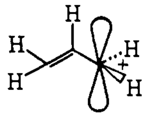

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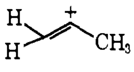

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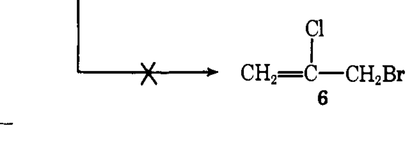
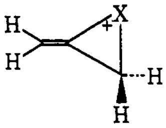
A note by Peer,[3] however, reported the addition of bromine chloride to allene to give 2-bromo-3-chloropropene (**5**) rather than the isomeric material (**6**) expected if the addition followed the same orientation as that of the hydrogen halide additions. This behavior is explicable if one postulates bridging by halogen (**7**) as a means of stabilizing the intermediate twisted allyl cation. Addition of the nucleophile to **7** could take place in either conjugate or normal fashion (S_N2) shown in Schemes I and II, respectively.



5

6



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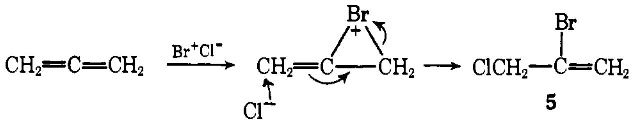
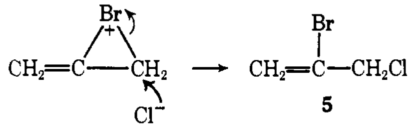
Scheme I



Scheme II



Peer proposed that 2,3-dichloropropene (**8**) and propargyl chloride (**9**) obtained by chlorination of allene in CH_2Cl_2, $CHCl_3$, and *sym*-$C_2H_4Cl_2$ arise from a "propadiene-Cl^+ complex" (**10**). This complex could lead directly to **8**. A "four-center elimination reaction" involving **11** was suggested for the formation of **9**.

Waters and Kiefer[4] have investigated the methoxymercuration of allenes. The reaction of allene with methanolic mercuric acetate produced only one product,

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[1] (a) Part XCV: G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 6883 (1969); (b) presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969; (c) undergraduate research participant.

[2] D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967).

[3] H. G. Peer, *Rec. Trav. Chim. Pays-Bas*, **81**, 113 (1962).

[4] W. L. Waters and E. F. Kiefer, *J. Amer. Chem. Soc.*, **89**, 6261 (1967).